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- 25 (54) Title of the Invention: **Bleach Composition**
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SPECIFICATION

1. Title of the Invention

Bleach Composition

5 2 Claims

1. A bleach composition, characterized by comprising:
a bleaching agent base of hydrogen peroxide or a peroxide that releases hydrogen
peroxide in aqueous solution; and
a bleaching activator consisting of sulfamic acid and/or a water-soluble salt of sulfamic
10 acid, and a hypohalogen acid and/or a water-soluble salt of a hypohalogen acid.

2. A bleach composition according to Claim 1, wherein the sulfamic acid and/or a water-soluble salt of sulfamic acid and the hypohalogen acid and/or a water-soluble salt of a hypohalogen acid are used in a proportion of 0.5-5 mol of the latter per 1 mol of the former.

3. A bleach composition according to Claim 1 or 2 comprising a binary system of an agent
15 (A) based on hydrogen peroxide or a peroxide that releases hydrogen peroxide in aqueous solution, and an agent (B) based on a bleaching activator consisting of sulfamic acid and/or a water-soluble salt of sulfamic acid, and a hypohalogen acid and/or a water-soluble salt of a hypohalogen acid.

3 Detailed Description of the Invention

20 Field of Industrial Utilization

The present invention relates to a bleach composition for use in various commercial and other applications, and more particularly to a bleach composition that causes minimal fading and discoloration of colored or patterned fabrics, and that can bleach treated articles rapidly, even at low temperatures.

25 Prior Art and Problems Which the Invention Is Intended to Solve

Bleaching agents include reducing type bleaching agents and oxidizing type bleaching agents; oxidizing type bleaching agents enjoy widespread use owing to their great effectiveness. The oxidizing type bleaching agents may be broadly classified as chlorine bleaching agents and oxygen bleaching agents. Disadvantages of chlorine bleaching agents include unsuitability to
30 colored/patterned fabrics due to discoloration/fading of the article being treated, and a

characteristic odor. Oxygen bleaching agents, on the other hand, have a wider range of use than do chlorine bleaching agents, lack the characteristic odor of chlorine bleaching agents, and are easy to use.

However, of the oxygen bleaching agents, the bleaching action of hydrogen peroxide, percarbonates, perborates, and adducts (e.g., pyrophosphate, citrate, sodium sulfate, urea, sodium silicate, etc.) of hydrogen peroxide that release hydrogen peroxide in aqueous solution is inferior to that of the chlorine bleaching agents, so bleaching treatment of short duration does not afford adequate bleaching effect. A particular drawback is the extended treatment time required to achieve adequate bleaching effect at low temperatures.

Accordingly, in the conventional art, bleaching activators, such as TAED (tetraacetyl ethylenediamine), TAGU (tetraacetyl glycol urile), PAG (pentaacetyl glucose), and cyanamide, are used concomitantly with hydrogen peroxide or other peroxides in order to enhance bleaching effect. However, the activating effect of these conventional bleaching activators is not always adequate for practical purposes. Specifically, those giving excellent bleaching effect tend to discolor or fade colors and patterns, while those not producing discoloration and fading tend to have inadequate bleaching effect. Thus, there is not currently available any practicable bleaching activator through which the advantages of oxygen bleaching agents may be realized.

The present invention was developed with the foregoing in view, and has as an object to provide a bleach composition offering exceptional bleaching effect, affording good bleaching of treated articles at low temperatures for brief periods, and causing no fading or discoloration of colored or patterned fabrics.

Means Used to Solve the Problems and Operation of the Invention

As a result of thoroughgoing research conducted with the goal of achieving the stated object of enhanced bleaching power without any loss of the benefits of oxygen bleaching agents, the inventors made the unexpected discovery that hypohalogen acids, when in the presence of sulfamic acid, enhance the bleaching power of hydrogen peroxide without causing fading or discoloration of colored or patterned fabrics, and thereby perfected the present invention.

Specifically, while hypohalogen acids and hydrogen peroxide have been used independently as bleaching agents in the conventional art, and have their own individual qualities, no bleaching agent that combines the two in a single bleaching bath has been

commercialized. This is due to the fact that when the two are simply combined in aqueous solution, a vigorous reaction ensues whereby oxygen gas is released, resulting in ineffective bleaching activation of the two components and in depressed bleaching power.

In the course of conducting an investigation of activation methods for oxygen bleaching agents, the inventors made the discovery that, where sulfamic acid and/or a water-soluble salt thereof is also present, concomitant use in aqueous solution of a hypohalogen acid and/or a water-soluble salt thereof with hydrogen peroxide or a peroxide that releases hydrogen peroxide in aqueous solution does not give rise to the aforementioned problem seen when a hypohalogen acid and/or a water-soluble salt thereof is simply mixed with hydrogen peroxide or a peroxide that releases hydrogen peroxide in aqueous solution, exceptional bleaching power is achieved, and good bleaching effect devoid of fading or discoloration of colored or patterned fabrics is afforded.

The present invention provides a bleach composition comprising a bleaching agent base of hydrogen peroxide or a peroxide that releases hydrogen peroxide in aqueous solution; and a bleaching activator consisting of sulfamic acid and/or a water-soluble salt of sulfamic acid, and a hypohalogen acid and/or a water-soluble salt of a hypohalogen acid.

The invention is described in greater detail below.

As noted, the bleach composition which pertains to the present invention contains a bleaching agent base of hydrogen peroxide or a peroxide that releases hydrogen peroxide in aqueous solution, and contains as a bleaching activator sulfamic acid and/or salt and a hypohalogen acid and/or salt. These three constituents, i.e. hydrogen peroxide or a peroxide that releases hydrogen peroxide in aqueous solution, sulfamic acid and/or salt, and hypohalogen acid and/or salt, are essential constituents. The absence of hydrogen peroxide or a peroxide will result in appreciable of fading or discoloration of colored or patterned fabrics, while the absence of sulfamic acid and/or salt and hypohalogen acid and/or salt will result in depressed bleaching power, and in either event the objects of the invention will not be attained.

In preferred practice, the bleach composition of the invention will be prepared as a binary system comprising an agent (A) based on hydrogen peroxide or a peroxide that releases hydrogen peroxide in aqueous solution, and an agent (B) based on a bleaching activator consisting of sulfamic acid and/or a water-soluble salt of sulfamic acid, and a hypohalogen acid and/or a

water-soluble salt of a hypohalogen acid. This allows the synergistic effects of the three constituent to be expressed in a reliable manner. Agent (A) and agent (B) may be in granular or liquid formulations.

5 The bleaching agent base used in the invention is hydrogen peroxide or a peroxide that releases hydrogen peroxide in aqueous solution. Any peroxide that releases hydrogen peroxide in aqueous solution may be used provided that it releases hydrogen peroxide upon dissolving in water; examples are any one or more of the following: hydrogen peroxide, percarbonates, perborates, and adducts (e.g. pyrophosphate, citrate, sodium sulfate, urea, sodium silicate, etc.) of hydrogen peroxide. In preferred practice, hydrogen peroxide, a percarbonate
10 (e.g. sodium percarbonate), or a perborate (e.g. sodium perborate monohydrate) will be used.

The sulfamic acid and/or salt used as a bleaching activator in the present invention is sulfamic acid and/or a water-soluble salt of sulfamic acid. Examples of water-soluble salts of sulfamic acid are sodium sulfamate, potassium sulfamate, ammonium sulfamate, magnesium sulfamate, calcium sulfamate, barium sulfamate, zinc sulfamate, etc. Especially preferred are
15 those which readily dissolve in cold water, e.g., sodium sulfamate, ammonium sulfamate, and magnesium sulfamate. Sulfamic acid and/or its salts may be used individually or in combinations of two or more.

Hypohalogen acids and/or salts include hypohalogen acids and water-soluble salts thereof. Examples of hypohalogen acids are hypochlorous acid, hypobromous acid, etc.
20 Examples of and water-soluble salts of hypohalogen acids are sodium hypochlorite, calcium hypochlorite, bleaching powder, sodium hypobromite, etc. For bleach composition formulations for household use, calcium hypochlorite or bleaching powder are favorable due to relatively good stability at high temperatures. Hypohalogen acids and/or their salts may be used individually or in combinations of two or more.

25 In preferred practice, the sulfamic acid and/or salt and the hypohalogen acid and/or salt are used in a proportion of 0.5-5 mol (preferably 0.8-2 mol) of the latter per 1 mol of the former. Where the proportion of sulfamic acid and/or salt per 1 mol hypohalogen acid and/or salt is less than 0.5 mol, adequate bleaching effect is not achieved in some cases.

The bleach composition of the invention may additionally contain suitable pH modifiers,
30 surfactants, enzymes, perfumes, blue tinting matter, etc. Where the bleach composition takes the

form of a binary system consisting of agent (A) and agent (B) described earlier, these optional constituents may be incorporated into agent (A), agent (B), or both.

In preferred practice, the composition of the present invention will take the form of a binary system consisting of agent (A) and agent (B). In preferred practice, agent (A) and agent (B) of such a binary system will be stored separately prior to use.

One suitable method for bleaching a treated article using the bleach composition of the invention involves preparing an aqueous solution of sulfamic acid and/or a water-soluble salt of sulfamic acid, and a hypohalogen acid and/or a water-soluble salt of a hypohalogen acid; mixing this aqueous solution with hydrogen peroxide aqueous solution or a peroxide that releases hydrogen peroxide in aqueous solution to prepare a bleach liquid; and then immersing the article to be treated (fibers, textiles, etc.) in the bleach liquid to effect bleaching treatment. Thus, where the composition takes the form of a binary system consisting of agent (A) and agent (B), if agent (B) is of non-liquid type (e.g. granules, etc.), the preferred method will be to first dissolve agent (B) in water and then add agent (A) thereto. Where agent (B) is liquid, agent (A) and agent (B) may be added to the water simultaneously, or one added to the water, followed by the other.

In preparation of a bleach liquid, the hydrogen peroxide/peroxide concentration is not critical; when preparing a bleach liquid for typical household use, however, a hydrogen peroxide solution [of a concentration] equivalent to 0.01-0.2 wt% is preferred. Since the bleaching activator is intended to enhance the bleaching effect of the hydrogen peroxide, large excess or excessively small amounts thereof with respect to the hydrogen peroxide are not practical; in preferred practice, the amount will be 0.1-2 mol (preferably 0.2-1 mol) hypohalogen acid and/or salt per 1 mol of hydrogen peroxide. For a composition of a binary system consisting of agent (A) and agent (B), it is favorable in terms of ease of use to package agents (A) and (B) in containers provided with a measuring cap, etc.

Effects of the Invention

As described in the preceding, the bleach composition which pertains to the present invention affords fast bleaching treatment of articles for treatment, even at low temperatures, with minimal discoloration or fading of colors and patterns.

The invention is described in greater detail through the following examples and comparative examples; these examples are not limiting of the invention.

Bleaching effect tests and discoloration/fading tests of the bleach compositions used in the examples and comparative examples were conducted using the following methods.

Bleaching Effect Test

5 (1) Test Fabric Pretreatment

Plain woven cotton fabric (#100) was laundered for 15 minutes in a washing machine using a commercially available detergent (BLUE DAIYA®) (bath ratio 30; 50°C) and then put through the spin cycle for 5 minutes. Washing and spinning were conducted again following this same procedure. Next, the fabric was overflow-rinsed for 15 minutes and put through the spin cycle for 5 minutes. Overflow rinsing and spinning were repeated a total of 5 times. The fabric was then air-dried to give a pretreated fabric.

(2) Preparation of Test Fabric

A 2% solution of black tea was boiled for 5 minutes. The pretreated fabric was immersed therein (bath ratio 30), boiled for 30 minutes, and then left standing for 30 minutes at 40°C. The fabric was then air-dried to give a test fabric (tea stained fabric).

(3) Bleaching Treatment

The tea [stained] fabric was immersed in a prepared bleach solution (bath ratio 100) and left standing for a predetermined time interval (30 minutes) at predetermined temperature (5°C or 20°C). The treated test fabric was spun for one minute in a washing machine, followed by overflow rinsing for one minute and spinning for one minute. The fabric was then ironed to give a bleached fabric.

(4) Bleaching Effect

A photoelectric reflectance photometer (ELREPHO by Carl Zeiss) was used to measure the reflectance of the pretreated fabric, tea stained fabric, and bleached fabric. Bleaching effect was calculated using the following equation:

bleaching effect =

$$\frac{[(\text{bleached fabric reflectance} - \text{tea stained fabric reflectance})]}{$$

$$(\text{pretreated fabric reflectance} - \text{tea stained fabric reflectance})] \times 100$$

Discoloration/Fading Test

(1) Test Fabric Pretreatment

Pretreatment of the test fabric was conducted as in the Bleaching Effect Test.

(2) Preparation of Dyed Fabric

- 5 0.75 g dye (C.I. No. Reactive Red-21) and 13.5 g anhydrous sodium sulfate were dissolved in 450 mL water. The pretreated fabric was immersed therein (bath ratio 30) and held for 20 minutes at 60°C. 9 g sodium carbonate was added and the fabric was held for an additional 60 minutes at 60°C. After washing with water, the fabric was washed with 0.1% acetic acid aqueous solution and then boiled for 5 minutes in a 0.2% anionic surfactant aqueous solution, washed with water, and dried to give a dyed fabric.

(3) Discoloration/Fading Treatment

Conducted analogously to bleaching treatment in the Bleaching Effect Test, using the dyed fabric instead of the tea stained fabric. Treatment temperature was 40°C. The resultant fabric was designated as discolored/faded fabric.

15 (4) Measuring Discoloration/Fading

A color difference meter (Z-Σ80, Nippon Denshoku Kogyo) was used to measure the lightness, hue, and saturation of the dyed fabric and the discolored/faded fabric.

Discoloration/fading (ΔE) was computed using the following equation:

20
$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

ΔL : change in dyed fabric lightness with bleaching

Δa , Δb : change in dyed fabric hue, saturation with bleaching

- (A higher value for a represents greater red intensity, and a lower value represents greater green intensity. A higher value for b represents greater yellow intensity, and a lower value represents greater blue intensity.)

A discoloration/fading value (ΔE) of 5 or above in the test represents discoloration/fading of an extent noticeable to the naked eye; in practical terms, this represents a high degree of discoloration/fading.

Example 1, Comparative Example 1

Granular agents (A) and granular agents (B) having the formulations indicated in Table 1 were prepared through powder blending. Bleach solutions were prepared by adding 20 g of agent (B) to 2 L of tap water at various temperatures (5°C, 20°C, 40°C), stirring for 5 minutes, and then adding 20 g of agent (A) to the solution and dissolving. Tests of bleaching effect were conducted at 5°C and 20°C using these bleach solutions. Discoloration/fading tests were conducted by the preceding method using 40°C bleach solution. Results are given in Table 1.

Table 1

Test Material		Invention										Comparison		
		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10	No. 11		
Formulation (wt%)	Agent (A)	sodium percarbonate	35.5%	53.7%	15.0%	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10	No. 11	
		sodium perborate	2.0	2.0	1.0	30.0%	40.0%	32.4%	30.0%	35.5%	35.5%	35.5%		
		sodium dodecylbenzenesulfonate		3.5		4.0	45.0	5.0	2.0	2.0	2.0	2.0	2.0	
		calcium sulfate hemihydrate		1.5			3.0	2.0						
		enzyme (ALKALASE 2.0T, NOVO)		0.2	0.2			0.1	0.1					
	Agent (B)	fragrance	balance	balance	balance	balance	balance	balance	balance	balance	balance	balance	balance	
		sodium carbonate												
		total	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	
		sodium sulfamate	40.0%			39.0%	4.5%							
		ammonium sulfamate		27.6%	33.0		4.5	50.0%	54.0%					
Test Eval.	Bleaching effect (%)		24.5	18.7	52.0	31.0	6.0	33.8	16.0	24.5%			24.5	
			0.5	0.5		0.2		2.5		0.5	0.5	0.5	0.5	
			balance	balance	balance	balance	0.1	balance	balance	balance	balance	balance	balance	
			100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	
			62	68	50	52	55	59	60	29	35	32	59	
	Discoloration/fadin g (ΔE)		73	81	61	69	65	71	74	27	45	46	65	
			2.5	2.6	2.6	2.2	2.0	3.3	2.0	3.3	2.9	2.4	22.8	

As will be apparent from the results in Table 1, the bleach formulation (blank) of Comparative Example No. 10 (devoid of both sulfamate and hypohalogen acid salt) exhibited bleaching effect of 32% at 5°C and 46% at 20°C; while there was virtually no discoloration (discoloration value $\Delta E = 2.4$), bleaching effect was poor. Similarly, [the bleach formulation of] Comparative Example No. 8 (containing no sulfamate) and [the bleach formulation of] Comparative Example No. 9 (containing no hypohalogen acid salt) also had poor bleaching effect. On the other hand, the bleach composition of Comparative Example No. 11 (containing both sulfamate and a hypohalogen acid salt but devoid of sodium percarbonate and sodium perborate) produced noticeable discoloration/fading.

In contrast, bleach compositions in accordance with the invention (No. 1-No. 7) all exhibited bleaching effect of 50% or above at 5°C and 60% or above at 20°C, high values for bleaching effect relative to the blank. Further, discoloration/fading was in each case such that ΔE was 4.0 or lower, indicative of bleach compositions having both excellent bleaching effect and no discoloration/fading.

Example 2, Comparative Example 2

Granular agents (A) and liquid agents (B) having the formulations indicated in Table 2 were prepared. Bleach solutions were prepared by adding 20 g of agent (A) to 2 L of tap water at various temperatures (5°C, 20°C, 40°C), adding 20 g of agent (B), and stirring. Following the methods described previously, tests of bleaching effect were conducted using 5°C and 20°C bleach solutions, and discoloration/fading tests were conducted using 40° bleach solution. Results are given in Table 2.

Test Material			Invention								Comparison		
Formulation (wt%)	Agent (A)	Agent (B)	No. 12	No. 13	No. 14	No. 15	No. 16	No. 17	No. 18	No. 19	No. 20		
			No. 12	No. 13	No. 14	No. 15	No. 16	No. 17	No. 18	No. 19	No. 20		
	Agent (A)		sodium percarbonate	100.0%									
			sodium perborate										
			Polyoxyethylene (P=8) nonyl phenyl ether		50%	50%		10%		80%	80%		
			sodium citrate, anhydrous		1.0			5					
			enzyme (ALKALASE 2.0T, NOVO)					0.5					
	Agent (B)		frangence										
			sodium carbonate		0.1	0.1	0.2	0.1	3.0%	3.0	3.0		
			total		balance	balance	balance	balance	1.0	1.0	1.0		
			sulfamic acid	100.0%	100.0%	100.0%	100.0%	100.0%	0.1	0.1	0.1		
			sodium sulfamate						balance	balance	balance		
Test Eval.	Bleaching effect (%)		magnesium sulfamate	10.0%	10.0%	10.0%	10.0%	10.0%	100.0%	100.0%	100.0%		
			calcium sulfamate						10.0%	10.0%	10.0%		
			potassium hypochlorite	5.0				5.0					
			sodium hypobromite										
			sodium hypochlorite		6.0	5.0	4.0	5.0	6.0	2.0	6.0%		
	Discoloration/fadin g (ΔE)		NES-D*		2.0	balance	2.0	balance	2.0	balance	2.0		
			water		balance	balance	balance	balance	balance	balance	balance		
			total	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%		
			5°C	70	70	65	57	57	58	39	37		
			20°C	85	84	78	65	68	62	51	36		
			40°C	2.7	2.9	2.6	2.5	2.7	27.1	2.6	3.6		

*NES-D: polyoxyethylene (P=10) nonyl phenyl ether sulfonate

As will be apparent from the results in Table 2, bleach compositions in accordance with the invention (No. 12-No. 17) all exhibited bleaching effect of 52% or above at 5°C and 64% or above at 20°C, with discoloration/fading in each case being such that ΔE was 3 or lower, indicative of bleach compositions having both excellent bleaching effect and no discoloration/fading. In contrast, the composition of Comparative Example No. 18 (devoid of sodium percarbonate and sodium perborate) exhibited bleaching effect but produced noticeable discoloration/fading; [the bleach formulations of] No. 19 and No. 20 (devoid of both sulfamate and hypohalogen acid salt) exhibited produced no discoloration/fading, but bleaching effect was poor.

In Example 2, the order in which agent (A) and agent (B) were added during bleach solution preparation was reversed; no appreciable difference in terms of bleaching effect resulted. Thus, it was verified that, where agent (B) is of liquid type, the order in which agent (A) and agent (B) are added does not affect bleaching effect.

Example 3

Bleach solutions were prepared by adding 70 g of sodium sulfamate and 43 g sodium hypochlorite to 2 L of tap water at various temperatures (5°C, 20°C, 40°C), stirring for 3 minutes, adding 200 mL 5% hydrogen peroxide aqueous solution to the resultant solutions, and stirring. Following the methods described previously, tests of bleaching effect were conducted using 5°C and 20°C bleach solutions, and discoloration/fading tests were conducted using 40° bleach solution.

Bleaching effect was 70% at 5°C and 84% at 20°C, indicative of excellent bleaching effect. ΔE was low (2.5) with no visible discoloration or fading.